



Study on the preheating stage of low rank coals liquefaction: Product distribution, chemical structural change of coal and hydrogen transfer



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ABSTRACT

Preheating stage of direct liquefaction of Yunnan lignite (YN) and Hami sub-bituminous coal (HM) in tetralin at temperature range of 200–350 °C was investigated under nitrogen atmosphere. In order to reveal the product characteristics and hydrogen transfer between coal and solvent during preheating process, thermo-gravimetric analyzer coupled with mass spectrometer (TG–MS), X-ray photoelectron spectroscopy (XPS) and gas chromatography coupled with mass spectrometer (GC–MS) were employed. The results show that yields of light products, i.e., oil, gas, and water, increase with raising temperature during the preheating process. YN and HM achieve 51.69% and 44.19% (daf) light products yields at 350 °C, respectively. Moreover, oxygen-containing functional groups, such as carboxyl, ethers, and alcohols in raw coal are reduced after preheating. In addition, hydrogen transfer achieves a perceptible extent even at 200 °C and the amount of transferred hydrogen increases with raising temperature. A positive dependence of hydrogen transfer on conversion is observed during preheating stage. Comparing the two coal samples, YN obtains higher conversion and hydrogen transfer due to its higher thermal reactivity at this temperature range. However, HM achieves higher oil yield than YN does at 350 °C since high hydrogen transfer amount and H/C ratio of raw coal promote the oil yield.

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1. Introduction

The utilization of low rank coals is limited by the high content of oxygen and low calorific value, in spite of the abundant reserves in world [1]. However, due to the high reactivity and H/C ratio, low rank coals can efficiently convert into oil and other fine chemicals with the process of direct coal liquefaction [2–6]. The direct liquefaction processes have been developed to moderate the conditions and increase the liquid yield [7]. The commercialized direct liquefaction process in China (Shenhua, Inner Mongolia) is depicted as follows. The feedstock of liquefaction, coal-oil slurry prepared by mixing pulverized coal and hydrogen donor solvent homogeneously, is pumped to a preheater and liquefaction reactor successively [8,9]. The preheating stage is required due to it can achieve less energy consumption and more liquid products [10–12]. In this stage, coal-oil slurry undergoes several changes. As described in previous publications [13,14], extraction of coal has taken place when slurry is pumped to the preheater, then extract yield increases with increasing temperature. Meanwhile, a number of labile

functional groups in coal are broken [15,16]. The broken fragments of coal can be converted into preasphaltene, asphaltene, and oil during the preheating stage [9]. Subsequently, the unreacted coal converts into light products at higher temperature [17]. In our previous work, the chemical structure and pyrolysis reactivity of coal in non-polar solvent tetralin have been preliminarily studied [15]. It shows that tetralin treatment was effective in dewatering and upgrading of low rank coal. During this process, the structure of unreacted coal was changing with deoxygenation and the thermal reactivity became lower. The change of coal structure would have impact on the subsequent reactions [18, 19]. However, the hydrogenation effect was not considered due to the neglect of light liquid product. Study on chemical characteristics of unreacted coal in the preheating stage is insufficient. In addition, the effect of chemical structural change on liquefaction conversion is unclear.

Hydrogen transfer from solvent or gas phase H₂ to coal-derived fragments is a necessary step for coal liquefaction. Previous publications [20–22] have reported that hydrogen transfer reactions occur at the preheating stage, and the hydrogen transfer amount from solvent or gas phase H₂ to coal is affected by temperature. Meanwhile, light products are formed under the hydrogen transfer effect. Researchers have demonstrated that hydrogen transfer amount is correlated with oil

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yield and liquefaction conversion in liquefaction reaction [23–25]. However, their relation in the preheating stage, which would reveal the hydrogenation level of coal and offer reference to determine the preheating condition, has been little focused. Besides, the hydrogen transfer amount is related to coal rank. Low rank coals achieve higher hydrogen transfer amount than that of high rank coals at same temperature. In addition, more radicals are generated through bond cleavage in low rank coals at same condition [26], which suggests that the thermally induced fragments promote the hydrogen transfer amount. As temperature impacts on both of fragment formation rate and hydrogen transfer rate, the selection of temperature is important for different ranks of coal preheating process.

The objective of this work is to explore the product distribution and hydrogen transfer of low rank coals at different preheating temperature during liquefaction. The experimental operating at preheating stage was simulated in a batch autoclave reactor with tetralin as solvent at 200–350 °C. Two Chinese low-rank coals, one lignite and one sub-bituminous coal, were used in this work. And the characteristics of products after preheating were examined to reveal the change of coal and tetralin at various temperatures. The experiments were conducted with N₂ as working atmosphere in order to rule out the effect of hydrogen transferring from gas phase to coal samples and focus on the hydrogen donating role of solvent.

2. Experimental section

2.1. Materials

Two low rank coals, Yunnan lignite (YN) and Hami sub-bituminous coal (HM), were used in this work. The coal samples were grounded and sieved to <150 μm, dried in a vacuum oven at 80 °C for 24 h before using. The proximate and ultimate analyses of the two coals are listed in Table 1. The solvents including tetralin (purity ≥ 99.0%), *n*-hexane (purity ≥ 98.0%), diphenyl (purity ≥ 99.5%), tetrahydrofuran (purity ≥ 99.0%) were commercially pure chemical reagents and used without further purification.

2.2. Preheating treatment

In each run, 5.00 g coal (dry basis) and 10.00 g tetralin were packed into 100 mL autoclave (Parr 4598, USA), which was then charged with N₂ to 3 MPa (cold pressure) after leak-checking. The reactor was heated from ambient temperature to the desired temperature (200–350 °C) at 5 °C/min with stirring rate of 400 rpm simultaneously. It was kept at the final temperature for 120 min before stopping heating. The gaseous products were collected in a gas bag and analyzed by a gas chromatograph (GC-950, Haixin, China). A 5A sieve column with TCD detector was used to detect H₂, N₂, CH₄, and CO. An Al₂O₃ column and carbon

sieve column with FID detector were used to analyze C₁–C₄ hydrocarbons and CO, CO₂, respectively. The solid-liquid mixture was totally transferred to a Soxhlet apparatus and extracted with *n*-hexane for 24 h. The extraction included tetralin and its derivatives, and some light products from coal conversion. And these light products were named as oil in this work. Then *n*-hexane was removed from extraction by vacuum rotary evaporation, and the remaining tetralin and its derivatives and oil were analyzed without further separation. The *n*-hexane insoluble solid was dried in a vacuum oven at 80 °C for 12 h, which was weighted to calculate the solid yield by using Eq. (1). Each run was repeated at least 3 times to ensure the duplicability, and the deviations were <2%. The solid samples obtained at 200–350 °C were named as YN-200 or HM-200; YN-250 or HM-250; etc. respectively. The solid samples were further extracted with tetrahydrofuran (THF) for 24 h to separate preasphaltene and asphaltene (PAA). PAA yield was calculated by using Eq. (2). The THF insoluble fraction was named as residue, and the conversion of coal during preheating process was calculated by using Eq. (3).

$$w_s = \frac{m_1}{m_c} \times 100 \quad (1)$$

$$w_p = \frac{m_1 - m_2}{m_c} \times 100 \quad (2)$$

$$c = 100 - \frac{m_2}{m_c} \times 100 \quad (3)$$

where, w_s is the solid yield (wt.%, daf); w_p is PAA yield (wt.%, daf); c is the conversion (wt.%, daf); m_1 is the weight of *n*-hexane insoluble solid fraction, g (daf); m_2 is weight of tetrahydrofuran (THF) insoluble fraction, g (daf); m_c is the weight of feed coal, g (daf).

Yield of water produced in the preheating process was determined by the oxygen mass balance in all products, as following Eq. (4):

$$w_w = 18 \times \frac{O_c - O_s - O_g - O_o}{16 \times m_c} \times 100 \quad (4)$$

where, w_w is the water yield (wt.%, daf); O_c , O_s , O_g , and O_o represent the content of oxygen in raw coal, solid, gas, and oil, respectively. The oxygen content in oil and solid were determined by using an elemental analyzer instead of by difference to obtain more accurate data.

Due to the relatively high boiling points of tetralin and naphthalene, some light oil would be also evaporated during the evaporation of solvent. The weight of residual oil would be lower than the actual value. Therefore, oil yield was obtained by difference as shown in Eq. (5):

$$w_o = 100 - w_s - w_w - w_g \quad (5)$$

where, w_o and w_g are the oil yield and gas yield (wt.%, daf), respectively.

2.3. Characterization

Thermo-gravimetric analyzer (TG, Setsys Evolution, SETARAM, France) coupled with a mass spectrometer (MS, Omnistar, Pfeiffer Vacuum) was used to study the pyrolysis behavior of raw coal. About 11 mg sample was placed in a corundum crucible and heated from 30 to 1050 °C at 10 °C/min in 100 mL/min argon atmosphere.

The chemical component of the solvent-oil mixture was identified and quantified by gas chromatography-mass spectrometer (GC-MS, ISQ, Thermo Scientific, USA). The samples were separated using a 30 m × 0.25 mm TR-5MS capillary column (Thermo Scientific, USA). Helium was employed as the carrier gas. The oven temperature was raised from 40 °C to 250 °C at 5 °C/min. The components were identified based on the attached library. Diphenyl was selected as internal standard to quantify tetralin and naphthalene.

The contents of carboxyl group in raw coal were determined by chemical method [27]. The aqueous determinations of acidity were

Table 1
Proximate and ultimate analyses of solid samples obtained at different temperatures.

Sample	Proximate analysis (wt.%)			Ultimate analysis (wt.%)					Atomic ratio	
	M _{ad}	A _d	V _{daf}	C _{daf}	H _{daf}	O _{daf} ^a	N _{daf}	S _d ^b	H/C	O/C
HM	6.94	6.76	54.19	74.35	5.61	18.68	1.07	0.27	0.91	0.19
HM-200	4.36	6.80	53.44	76.19	5.71	16.76	1.09	0.23	0.90	0.16
HM-250	3.55	6.95	52.47	77.42	5.77	15.47	1.11	0.21	0.89	0.15
HM-300	2.77	7.49	52.03	78.78	5.87	13.87	1.21	0.25	0.89	0.13
HM-350	1.55	10.23	48.78	81.34	5.89	11.00	1.46	0.28	0.87	0.10
YN	9.29	10.27	51.46	68.35	4.73	24.83	1.28	0.73	0.83	0.27
YN-200	5.24	10.73	49.85	71.30	4.84	21.72	1.36	0.71	0.81	0.23
YN-250	4.36	11.85	46.42	75.09	5.04	17.60	1.48	0.69	0.81	0.18
YN-300	2.94	12.94	45.34	77.60	5.17	14.89	1.57	0.67	0.80	0.14
YN-350	2.32	17.33	42.93	81.47	5.47	10.33	1.92	0.66	0.81	0.10

ad: air dry basis; d: dry basis; daf: dry ash free basis.

^a By difference.

^b Total S.

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